PHYSICAL REVIEW B VOLUME 33, NUMBER 6 15 MARCH 1986

Low-temperature thermal expansion and specific heat of KCl containing Li tunneling states

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(Received 16 September 1985)

Thermal-expansion coefficients and specific heats have been measured in the temperature range 0.1–10 K for KCl crystals containing less than 200 ppm ^{6}Li or ^{7}Li. The tunneling states associated with isolated Li ions give rise to a Grüneisen parameter of $\Gamma_{\mathrm{Li}} = +150 \pm 15$ which is isotropic and independent of temperature or of Li isotope.

I. INTRODUCTION

We report a study of the contribution by substitutional Li impurities to the thermal expansion and specific heat of KCl. The results are intended to complement, and assist, ongoing theoretical efforts directed to a better understanding of low-energy tunneling systems and their coupling to strain fields.

The low-lying energy levels arising from defects in solids have been the subject of considerable experimental and theoretical investigation for more than two decades.[1–3] In crystalline solids, these energy levels can occur if, instead of a single potential-energy minimum at the site of substitution, an atomic or molecular impurity finds two or more equivalent minima. Tunneling between the minima then splits the degenerate ground state into two or more closely-spaced energy levels separated by energies Δ_i. The Δ_i can be small compared to other excited energy levels of the impurity which therefore remain thermally inaccessible at low temperatures. The Δ_i are also small with respect to the Debye energies of the crystalline lattice making it possible, in many cases, to separate the tunneling behavior from that of the lattice phonons. Tunneling states influence most low-temperature properties of the crystalline host. A Schottky peak in the specific heat at a temperature of $T \approx 0.4\Delta$ is the most commonly recognized example of this influence when the defect concentration is small.

The coupling between a tunneling state and its environment can be measured by several techniques including that of thermal expansion.[4] Our interest will be in the average thermal expansion contributed by each impurity site. This normalized expansion is conveniently characterized by the Gruneisen parameter Γ given by an equation of the form[5] $\Gamma = 3\alpha B/C$, where α is the coefficient of linear thermal expansion, C is the specific heat, and B is the bulk modulus[6] of the host crystal. When it is intended that Γ be related *only* to a specific excitation, then the portions of α and C contributed by those sites alone should be used in the calculation of Γ. For example, the magnitude of Γ is ≈ 1 for more common excitations such as conduction electrons or thermal phonons.

For tunneling states, experimental values as large as 300 have been reported.[7] However, if one uses a theoretical model of the tunneling state which is adequate for other purposes and computes $\Gamma = -d(\ln\Delta)/d(\ln V)$, where V is volume, the result (see Sec. III) is generally $\Gamma \approx 10$. Therefore a considerable refinement of the model is needed,[8] a refinement which may be available through advanced computer techniques.[9] The present paper provides quantitative data for comparison with improved models.

The tunneling system KCl:Li was selected for our study for several reasons. The tunneling of a simple ion such as Li should simplify theoretical calculations. The tunnel splitting of $\Delta \approx 1$ K for the ground state is small relative to the energy ($\gtrsim 60$ K) of the higher levels. Therefore those energy levels of interest are nearly pure tunneling states, a fact which should further simplify computations. The tunneling splitting of $\Delta \approx 1$ K lies in an experimentally accessible temperature range, yet is small enough that the tunneling behavior will not be masked by thermal phonons. This last point is further enhanced by the large $\Gamma(\approx 300)$ reported[7] for Li in KCl. Finally, the large isotope effect available through the use of both ^{6}Li and ^{7}Li provides an additional test of any theoretical model.

Lithium is a substitutional defect in KCl, occupying a K site. The small Li ion lies off center along one of the eight equivalent $\langle 111 \rangle$ directions. Quantum tunneling between these potential minima splits the eightfold degenerate ground state into four energy levels having a degeneracy of 1-3-3-1. These four levels are nearly equally spaced in energy with $\Delta \approx 1.2$ K for ^{7}Li. For additional information on theoretical and experimental studies of KCl:Li (and on other tunneling systems) the reader is directed to Refs. 1–3.

II. EXPERIMENTAL TECHNIQUE AND RESULTS

Samples of KCl:Li were purchased from the Crystal Growth Laboratory of the University of Utah. The starting materials had been pretreated to reduce the OH$^-$ impurity concentration to less than 0.1 ppm. Because of segregation of Li in the melt, a Li concentration gradient occurs along the axis of growth. To minimize this gradient, large amounts of starting materials were used. In addition, samples were cut from 0.5 cm thick layers oriented perpendicular to the growth direction. Paired specific-heat and thermal-expansion samples were always cut from the same layer. The single exception was a sample having its long axis oriented along $\langle 111 \rangle$, which was used for both specific-heat and thermal-expansion measurements.

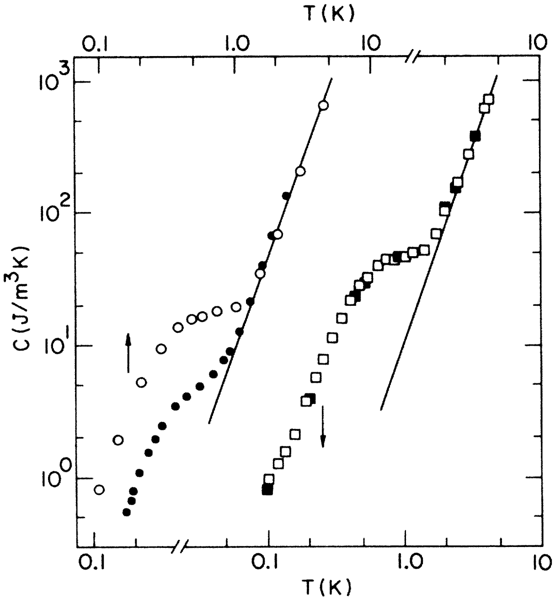

FIG. 1. Total specific heat C of sample 60^7Li (○, top scale) and sample 150^6Li (□■, two independent runs, bottom scale) versus temperature T. Also shown, by solid circles, are the earlier data of Ref. 11 on 20^7Li. The solid lines represent the T^3 phonon contributions.

The concentration n of Li in each sample was estimated from the specific-heat data by using the relation $nk(\ln 8) = \int (C/T)dT$. A sample having, for example, 60 ppm ^{7}Li (relative to K sites) will be designated for convenience as 60^7Li. The ^{7}Li introduced to the melt was a natural isotopic mixture containing 7% ^{6}Li, while the ^{6}Li introduced to the melt was reported to be $\approx 95\%$ ^{6}Li. This small admixture of isotopes does not significantly influence the results of the thermal-expansion or specific-heat measurements.

A total of four different Li concentrations were used in the measurements. Two of these, 60^7Li and 70^6Li, were nominally of the same concentration so as to observe the isotope effect. Another set, 70^6Li and 150^6Li were intended to check for the presence of a concentration dependence. A third combination, 150^6Li⟨100⟩ and 130^6Li⟨111⟩, was used to check the isotropy of the linear expansion coefficient.

In measuring the specific heat, the sample was clamped between dry sapphire plates to provide a long equilibration time (≈ 10 sec) between sample and refrigerator. A ≈ 5-msec heat pulse Q was applied via an electrical heater, and the temperature excursion ΔT was measured with a carbon resistance thermometer. The signal-to-noise ratio was enhanced by a single-averaging technique.[10] The specific heat was then computed using the relation $C = Q/V\Delta T$. In all cases, the addenda heat capacity was negligible ($< 1\%$).

The carbon-composition resistance thermometers used for the specific-heat (and thermal-expansion) measurements were calibrated *in situ* against three germanium resistance thermometers (for reliability). The germanium thermometers had been calibrated to an accuracy better than 1% on the EPT76 temperature scale against National Bureau of Standards superconducting fixed points using a cerium-magnesium-nitrate magnetic thermometer for interpolation. The absolute accuracy of a specific-heat measurement was $\approx 5\%$.

The specific-heat data for two of the samples are shown in Fig. 1 using offset temperature scales to separate the two sets of data. The set on the right contains results from two independent runs and illustrates the reproducibility of our data. The set on the left shows that the present data, in the phonon-dominated T^3 regime indicated by the solid line, are in good agreement with earlier results.[11]

To obtain the Li contribution C_{Li} to the specific heat, the phonon contribution must be subtracted. The phonon contributions for each sample are summarized in Table I together with the related Debye temperature Θ_D. The Θ_D for the 130^6Li and 150^6Li samples, cut from different layers of the same crystal, are $\approx 7\%$ smaller than for the other samples which were cut from other crystals. This difference is real, and may indicate a weak dependence of Θ_D on Li content.

The thermal expansion was measured using a dilatometer incorporating a superconducting quantum interference device (SQUID) detector which has been described previously.[12] An improvement in the dilatometer was the replacement of the earlier quartz-disk transducer with a small piezoelectric ceramic tube.[13] This change considerably improved the reproducibility of the transducer package which retains the calibration of the dilatometer between runs. The transducer is calibrated periodically in separate runs against the known thermal expansion of high-purity copper at $T \geq 2$ K. Since the output of this transducer is independent of temperature, the calibration can be reliably transferred to lower temperatures. The ab-

TABLE I. Summary of measured parameters for KCl crystals containing substitutional Li impurities. ⟨?⟩ indicates that the direction was not known.

	Pure	60^7Li	70^6Li	150^6Li	130^6Li
Sample axis	⟨?⟩	⟨100⟩	⟨100⟩	⟨100⟩	⟨111⟩
α_D/T^3 (10^{-11} K^{-4})	4.8±0.2[a]	5.8±0.4	5.4±0.5	7.0±0.4	4.8±0.3
C_D/T^3 (J/m^{3}K^4)	8.2±0.2[b]	7.9±0.3	8.4±0.3	10.0±0.3	10.0±0.3
Θ_D (K)	233[b]	236±3	231±3	218±3	218±3
Γ_D	+0.35[a]	+0.43	+0.38	+0.41	+0.29

[a] Reference 26 (for $T < 10$ K).

[b] Reference 11.

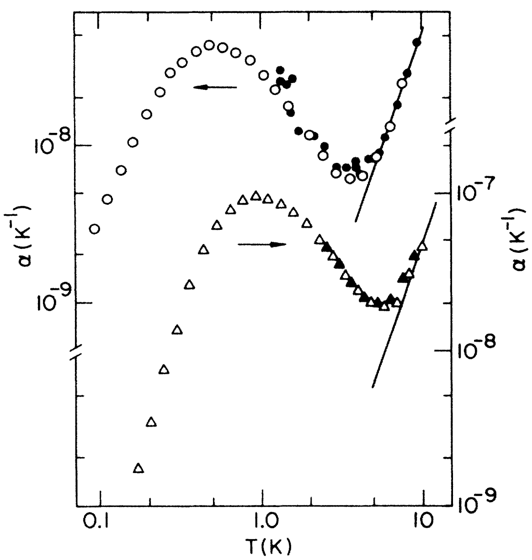

FIG. 2. Total linear thermal-expansion coefficient α of sample 60^7Li (○, ⟨100⟩, left scale) and sample 130^6Li (△▲, two independent runs, ⟨111⟩, right scale) versus temperature T. Also shown by solid circles are the earlier data of Ref. 7 on $\approx 100^7$Li. The solid lines represent the T^3 phonon contributions. The ^{6}Li-^{7}Li isotope effect is readily observed as a shift in the temperature of the peak, see text.

solute accuracy is still limited by the calibration procedure to $\approx 10\%$. Within a given run, the relative accuracy is 5%.

The thermal-expansion data for two samples are shown in Fig. 2 using offset vertical scales to separate the two data sets. The isotope effect, the shift in temperature of the peak occuring near ≈ 1 K, is apparent. The lower data set contains the results of two independent runs and indicates the reproducibility of our data. The upper set shows that our data are in agreement with earlier measurements[7] in the T^3 regime, represented by the solid line, where phonons dominate the expansion.

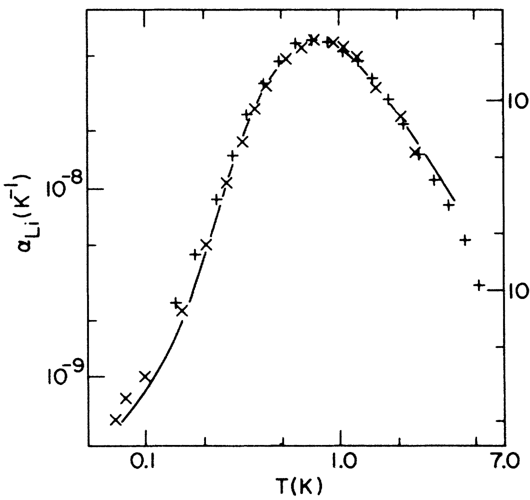

FIG. 4. Contribution of ^{6}Li impurities in sample 70^6Li to the thermal expansion (+ , ⟨100⟩, left scale) or specific heat (×, right scale). The solid curve is a theoretical fit to the *specific heat* as discussed in the text.

To obtain the contribution $\alpha_{\rm Li}$ of Li to the expansion coefficient, that contributed by the phonons must be subtracted. The phonon contribution α_D for each sample is included in Table I. The Gruneisen parameter Γ_D related to thermal phonons in KCl is $\approx +0.4$. Having subtracted these phonon contributions, the resulting $\alpha_{\rm Li}$ (and $C_{\rm Li}$) are shown in Figs. 3—6. Each figure has a thermal-expansion

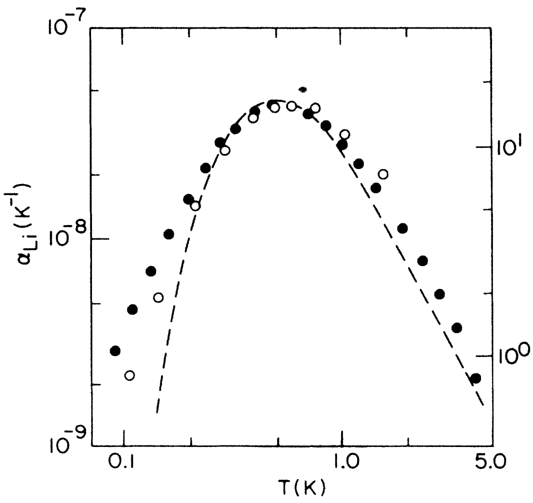

FIG. 3. Contribution of ^{7}Li impurities in sample 60^7Li to the thermal expansion α (●, ⟨100⟩, left scale) or specific heat (○, right scale). The dashed line is a 1-3-3-1 Schottky peak as discussed in the text.

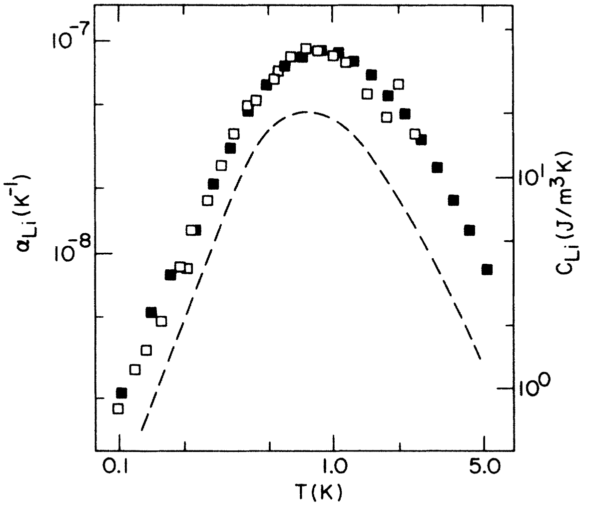

FIG. 5. Contribution of ^{6}Li impurities in sample 150^6Li to the thermal expansion (■, ⟨100⟩, left scale) or specific heat (□, right scale). The dashed curve represents the data for 70^6Li from Fig. 3.

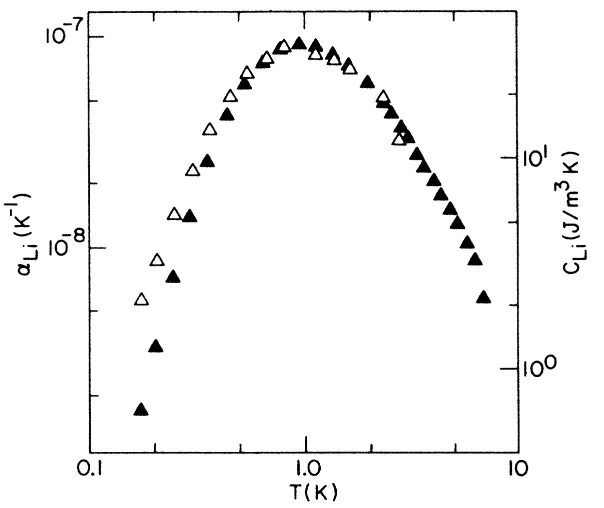

FIG. 6. Contribution of ^{6}Li impurities in sample 130^{6}Li to the thermal expansion (▲, $\langle 111 \rangle$, left scale) or specific heat (△, right scale).

scale on the left and a specific-heat scale on the right. In all figures, the same type of symbol has been used to represent data for a particular sample. In plotting Figs. 3–6, the C_{Li} data were shifted vertically until the maximum in the peak was superimposed on that for the α_{Li} data. This permits a more convenient comparison of the temperature dependence of α_{Li} relative to that of C_{Li}.

The Gruneisen parameters Γ_{Li} associated with the substitutional Li and obtained from Figs. 3–6 are shown in Fig. 7 as a function of temperature. To obtain the Γ_{Li}, smooth curves were constructed through the C_{Li} or α_{Li} data points for the purpose of interpolation.

III. DISCUSSION

We discuss first the data obtained above ≈ 0.5 K where, in Fig. 7, the Gruneisen parameter is isotropic and temperature independent with $\Gamma_{Li} = +150 \pm 15$ to within the combined accuracies of the α and C measurements. Note that Γ_{Li} has the same value for both Li isotopes. This is to be contrasted with the factor of 1.40 shift in peak temperature for the two isotopes at the same concentration (Figs. 3 and 4).

The Γ_{Li} may be compared[14] in Fig. 8 with values deduced from measurements of the change in tunnel splitting Δ with applied hydrostatic pressure,[15,16] that is, $\Gamma = -d(\ln\Delta)/d(\ln V)$. The two kinds of data are similar both in magnitude and in the absence of a significant isotope effect in Γ, but the high-pressure results would appear not to extrapolate linearly to our value of $\Gamma_{Li} = +150$ at zero pressure.

The data of Fig. 7 can also be compared with simple theoretical computations of Γ. For example, a model using isotropic off-center harmonic potential-energy wells[17] can reproduce the 1-3-3-1 tunneling-state energy levels with equal separations Δ. Assuming the bottom of the well (the "oscillator frequency") is unchanged by small strain, $\Gamma_{Li} = -d(\ln\Delta)/d(\ln V) \approx +20$ is obtained.[13] This value is typical of simple estimates of Γ for tunneling states,[18,19] and indicates the need for a more realistic microscopic model of such states. The same model would predict a 17% reduction in Γ when ^{6}Li is substituted for ^{7}Li. The $\approx 15\%$ uncertainty reflected in the results of Fig. 7 precludes a test of this prediction.

The values of Γ_{Li} at temperatures below ≈ 0.5 K in Fig. 7 diverge from the value $\Gamma_{Li} = +150$, and even appear to become anisotropic with a smaller Γ_{Li} along the $\langle 111 \rangle$ direction. To understand this result requires a closer scrutiny of the data presented in Figs. 3–6.

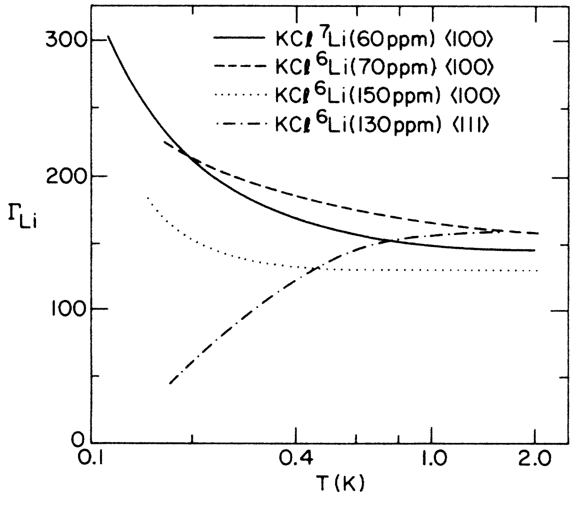

FIG. 7. Gruneisen parameter Γ_{Li}, related to the substitutional Li in KCl, versus temperature. The Gruneisen parameter serves to indicate the average thermal expansion contributed by a Li impurity.

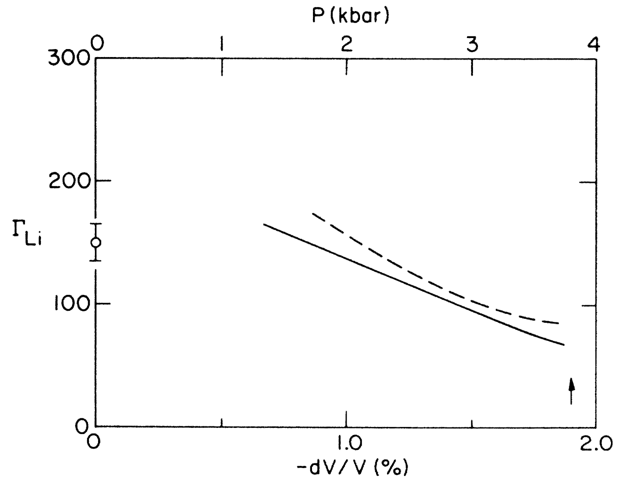

FIG. 8. Gruneisen parameter Γ_{Li} related to substitutional ^{6}Li (solid line) or ^{7}Li (dashed line) in KCl, versus hydrostatic pressure P or strain dV/V. The Li ion goes on center near the pressure indicated by the arrow. Information on the pressure dependence was obtained from Refs. 15 and 16, the zero-pressure value (o) is from Fig. 7.

The dashed curve in Fig. 3 represents a Schottky specific heat for four equally-spaced energy levels having a degeneracy of 1-3-3-1. The energy spacing was taken as $\Delta = 1.2$ K as deduced from earlier specific-heat measurements at lower Li concentration.[11] (An unequal energy spacing[20] would shift the curve $\approx 10\%$ lower in temperature.) The reader can observe that the measured peak in C_{Li} (the open circles) is broader than the theoretical peak. At 0.1 K, for example, the measured C_{Li} is a factor of 10 larger than the computed value. This is also true for the other data set of Figs. 4–6. It is difficult to produce the observed width by modifying the separations or degeneracies of the $\langle 111 \rangle$ tunneling state (by assuming, for example, tunneling to opposite $\langle 111 \rangle$ wells rather than to neighboring wells). Therefore it is assumed that not all Li sites are identical, that the broadened specific-heat peak results from a spectrum of tunneling states. This mechanism has been suggested previously,[1,2,21] and is consistent with other observations to be discussed below.

The spectrum of tunneling states could arise from interactions of the Li with local strain or electric fields. The density of dislocations required to produce the required strain fields can be estimated. Assume that the strain field of one dislocation is given by $b/2\pi R$, where b is the Burgers vector and R is the distance between a dislocation and a Li ion. Also, assume an average strain interaction of $\Gamma = 150$ as obtained from Fig. 7. The observed broadening would require $\approx 12\%$ of the Li concentration to have their Δ shifted downward by a factor of ≈ 2. This would require a dislocation density $\approx 3 \times 10^{13}$ m^{-2}, a value larger than that found in heavily deformed alkali-halide crystals. Densities in the as-grown condition are typically a factor of $\approx 10^3$ smaller. Therefore, it is unlikely that local strain fields cause the broadening indicated in Fig. 3.

An obvious source of local electric fields are the electric dipole moments,[22] $p \approx 5.5$ D, associated with the Li tunneling states. Evidence that Li-Li interactions are significant is found in Fig. 5. The dashed curve represents the data for sample 70^{6}Li having a factor 2 smaller Li concentration. The position of the maximum is seen to increase by $\approx 15\%$ with the increase of Li concentration. (This also is true for 130^{6}Li of Fig. 6.) In addition, the peak is further broadened by the addition of Li. Both of these effects suggest the presence of a Li-Li interaction. Since the elastic interaction between Li sites is negligible,[1] we will assume the relevant interaction is electric.

A rough estimate of the dipolar interaction can be made. Since the concentration of Li ions is small, we assume that pair interactions dominate, i.e., that the interaction energy is of the form $U \propto R^{-3}$, where R is the dipole-dipole separation. The tunnel splitting is then of the form[23] $\Delta = [(U^2 + 4\Delta_0^2)^{1/2} \pm U]/2$, where Δ_0 is the splitting in the absence of interaction.[24] We further assume that the probability distribution in U is determined by a statistical distribution in R, i.e., that the Li ions are sited at random in the KCl lattice. The net specific heat is then a spectrum of Schottky peaks having energies Δ. Summation of this spectrum gives the solid line of Fig. 4 which is to be compared with the $\times$ symbols. Similar fits are obtained for the other samples.[13] The spectrum in Δ has two consequences, namely a broadening in the peak and a shift of the peak to higher temperatures. In particular, the observed temperature dependence of C near and below 0.1 is explained (see also Ref. 21). Three adjustable parameters are employed. One is the concentration n of Li. The fits for all our samples required an n which was 4–10 % larger than that deduced from the measured entropy (see Sec. II). The second parameter was Δ_0, which was 1.25 K for ^{7}Li and 1.80 K for ^{6}Li. These values lie within 10% of previously reported values obtained at small n where interactions would be less important.[11] The third parameter is $U_0 = U(R = a)$, where a is the K-K distance in KCl. The value of U_0 was the same for all samples, $U_0 = 600$ K. This is the same order of magnitude as the interaction energy estimated from the relation $U_0 \approx p^2/4\pi\epsilon a^3 \approx 400$ K. Our coarse assumptions concerning pair interactions of tunneling states are probably inadequate, and the Li distribution may not be completely random in our KCl samples.[25] Nevertheless, the available evidence does indicate that the broadening of the specific-heat peak is caused by Li-Li interactions.

Returning now to the region of Fig. 7 lying at temperatures below ≈ 0.5 K, we speculate that the developing, apparent anisotropy in Γ_{Li} with decreasing temperature may be ascribed to a fraction of the Li population, perhaps $\approx 3\%$, which interact with neighboring Li sites.

The main conclusion of this paper is that the tunneling states associated with an *isolated* Li ion in KCl can be represented by an isotropic Gruneisen parameter of $\Gamma_{\text{Li}} = +150$ which is independent of temperature and of Li isotope.

ACKNOWLEDGMENTS

This research was supported by the Materials Science Division of the Department of Energy under Contract No. DE-AC02-76ER01198. The authors thank M. W. Klein for very helpful discussions.

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[1] V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. **42**, 201 (1970), and papers cited therein.

[2] F. Bridges, Crit. Rev. Solid State Sci. **5**, 1 (1975), and papers cited therein.

[3] *Amorphous Solids,* edited by W. A. Phillips (Springer, Berlin, 1981).

[4] F. W. Sheard, in *Thermal Expansion,* edited by M. G. Graham and H. E. Hagy (AIP, New York, 1971), p. 155.

[5] T. K. Barron, J. G. Collins, and G. K. White, Adv. Phys. **29**, 609 (1980).

[6] $B = (C_{11} + 2C_{12})/3 = 1.97 \times 10^{10}$ J/m^3 using values for the elastic constants C_{11} and C_{12} taken from M. H. Norwood and C. V. Briscoe, Phys. Rev. **112**, 45 (1958).

[7] C. R. Case, K. O. McLean, C. A. Swenson, and G. K. White, in *Thermal Expansion,* edited by M. G. Graham and H. E. Hagy (AIP, New York, 1971), p. 183.

[8] J. P. Sethna, Phys. Rev. B **25**, 5050 (1982).

[9] J. H. Harding, A. H. Harker, P. B. Keegstra, R. Pandy, J. M.

Vail, and C. Woodward, Physica (Utrecht) (to be published).

[10] G. J. Sellers and A. C. Anderson, Rev. Sci. Instrum. **45**, 1256 (1974).

[11] J. P. Harrison, P. P. Peressini, and R. O. Pohl, Phys. Rev. **171**, 1037 (1968).

[12] D. A. Ackerman and A. C. Anderson, Rev. Sci. Instrum. **53**, 1657 (1982).

[13] J. N. Dobbs, Ph.D. thesis, University of Illinois, 1985 (unpublished).

[14] B. Fischer and M. W. Klein, Solid State Commun. **35**, 37 (1980).

[15] A. M. Kahan, M. Patterson, and A. J. Sievers, Phys. Rev. B **14**, 5422 (1976).

[16] U. Holland and F. Luty, Phys. Rev. B **19**, 4298 (1979).

[17] M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. **153**, 1009 (1967).

[18] K. G. Lyon, G. L. Salinger, and C. A. Swenson, Phys. Rev. B **19**, 4231 (1979).

[19] G. J. Morgan, G. K. White, and J. G. Collins, Philos. Mag. B **43**, 1039 (1981).

[20] M. C. Hetzler and D. Walton, Phys. Rev. B **8**, 4801 (1973).

[21] P. P. Peressini, J. P. Harrison, and R. O. Pohl, Phys. Rev. **182**, 939 (1969).

[22] A. T. Flory, Phys. Rev. B **4**, 614 (1971).

[23] M. W. Klein, Phys. Rev. B **29**, 5825 (1984).

[24] Since the specific heat of a 1-3-3-1 tunneling system is identical to that of a properly normalized two-level system, we have approximated the interacting pair as an appropriately normalized set of two-level systems (see Ref. 13).

[25] N. Byer and H. S. Sack, J. Phys. Chem. Solids **29**, 677 (1968).

[26] G. K. White and J. G. Collins, Proc. R. Soc. London, Ser. A **333**, 237 (1973).